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The removal of atmospheric aerosols in a heavy industrial coastal city in China with frequent rainfall

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Rapid urbanization and heavy industrialization generally result in serious aerosol pollution. Contrary to this conventional wisdom, Zhanjiang, one industrial city in the southernmost point of the Chinese mainland, is not accompanied by aerosol pollution and its air quality index always ranks high compared to other cities in China. To investigate this contradiction, 72-hour total suspended particles (TSPs) and water-soluble inorganic ions (WSIIs; including Mg^{2+}, Ca^{2+}, K^{+}, Na^{+}, NH_4^{+}, Cl^{-}, NO_3^{-}, and SO_4^{2-}) were collected in Zhanjiang, China, from November 2018 to November 2019. The relative humidity (RH) was higher than 80% throughout the whole year in Zhanjiang. However, the TSPs and WSIIs were not correlated with RH, indicating that RH can increase the particle size, but this had a minor impact on the dry deposition rate. The larger particles induced by RH were easily captured by wet precipitation, leading to a seasonal pattern with higher TSP and WSII mass concentrations during the dry and cool season and lower values during the hot and rainy season. This seasonal pattern and high aerosol acidity indicate that TSPs, WSIIs, and acidic gaseous precursors from the local sources were preferentially scavenged by the abundant rainfall and high precipitation frequency. Principal component analysis (PCA) results suggest that relatively clean marine emissions and secondary aerosols were the most important sources of TSPs and WSIIs. Our results indicate that the inconsistency between the heavy industrial activities and excellent air quality in Zhanjiang may be related to the high precipitation frequency (63%) and the marine dilution effect (27%).

KEYWORDS

aerosol, air quality improvement, water-soluble inorganic ions, precipitation, sources, Zhanjiang City

Introduction

One consequence of the rapid urbanization and industrialization in developing countries is the increase in the total suspended particles (TSPs) in the atmosphere, i.e., air quality deterioration (Seinfeld, 2004; Huang et al., 2014). TSPs have long been regarded as a global air pollution concern due to their significant impacts on climate change, atmospheric chemistry, air quality, acidification, and human health (Fuzzi et al., 2015; Xiao et al., 2017). The TSPs (also called atmospheric aerosols) are primarily composed of various chemical species and water-soluble inorganic ions (WSIIs) (Ali-Mohamed, 1991). Therefore, observations of WSIIs may provide valuable information for controlling aerosol pollution.

Secondary inorganic aerosols, such as SO_4^{2-} and NO_3^- particles, are important contributors to the WSIIs in the TSPs (Guo et al., 2014). The SO_4^{2-} and NO_3^- particles in the atmosphere are mainly generated from oxidation of their representative gaseous precursors (SO_2 and NOx) emitted from ambient fossil fuel combustion (Shon et al., 2012; Xu L. L. et al., 2017; Liu et al., 2019). These ions and gaseous precursors are largely linked to aerosol pollution and acidification (Cao et al., 2013; Weber et al., 2016; Liu et al., 2019; Tian et al., 2021). Previous studies have reported significant increases in the aerosol mass, which pose a potential threat to human health due to high fossil fuel combustion (Zhang et al., 2011). Additionally, Xiao and Liu (2004) found that air quality deterioration in Guiyang was caused by industrial activities, and some industries should be relocated to mitigate local haze pollution.

Zhanjiang city (20.00–21.58°N, 109.52–110.92°E), the site of our study, is located in Guangdong Province, southern China, and is a tropical coastal city close to the South China Sea (SCS,< 30 km). During the past decades, a variety of industries (especially heavy industries, i.e., petrochemical factory as well as iron and steel plant) have moved to and sprung up in Zhanjiang. Nowadays, Zhanjiang is a famous manufacturing and heavy industry base. According to the Guangdong Statistical Yearbook, the total output value of heavy industries above designated size in Zhanjiang accounts for ~50% of Zhanjiang's gross regional domestic product. Additionally, the Basf Zhanjiang Integrated Base, the Lianjiang Nuclear Power Plant, and the Jingxin Zhanjiang Donghai Thermal Power Plant are under construction. Marine pollution caused by the industrialization and urbanization *via* terrestrial input in this region has been recently reported (Sun et al., 2018; Peng et al., 2020; Li J. C. et al., 2020). However, the influence of industrialization and urbanization on ambient air quality in Zhanjiang are not reported and still needs to be clarified, as TSPs and WSIIs in the atmosphere can be captured by rainfall and then enter into the marine systems. This may pose a potential risk to marine systems, for example, eutrophication (Cui et al., 2020; Wang J. J. et al., 2020).

Although the sources and impact factors of the WSIIs in the TSPs have been studied extensively in order to lessen aerosol pollution (Xiao and Liu, 2004; Kundu et al., 2010; Zhang et al., 2011; Xiao et al., 2017; Wang Q. Q. et al., 2020), limited research has been conducted on the impact of precipitation on WSIIs, which is considered to be an important process for removing TSPs and soluble gases in the ambient atmosphere (Hou et al., 2018). Thus, we hypothesize that the shorter aerosol lifetime and shortage of gaseous precursors in the atmosphere caused by precipitation may contribute to reducing aerosol pollution, especially in tropical regions with frequent precipitation and plentiful rainfall.

To investigate this contradiction and to verify this speculation, we monitored the TSPs in the atmosphere for one year and analyzed the WSIIs in the TSPs in the tropical city of Zhanjiang, China. The objectives of this study are as follows: (1) to determine the TSP and WSII concentrations and seasonal variations; (2) to verify the aerosol removal effect of precipitation; and (3) to use principal component analysis (PCA) to identify the possible sources of the WSIIs.

Methods and materials

Sampling site and sample collection

Zhanjiang in the southernmost point of the Chinese mainland (Figure 1) has a typical tropical monsoon climate, with a cool dry season from October to March (dry season) and a hot wet season from April to September (rainy season; Chen et al., 2019). The average annual temperature and rainfall in the city is 23°C and 1689 mm, respectively (Chen et al., 2019). The sampling campaign was conducted from 1 November 2018 to 1 November 2019 at 1.5 m above the roof of a building in Guangdong Ocean University in rural Zhanjiang City (21.15°N, 110.30°E). The TSPs in the atmosphere were collected on a 450°C pre-baked quartz fiber filter (Type MK360, 203 x 254 mm, Munktell Filter, Sweden) using a high-volume air sampler (1.37 ± 0.25 m^3/min; KB-1000-180815, Xiamen, China), and the cumulative sampling time for each aerosol sample was about 72 hours. After sampling, the filter was stored at -20°C to prevent volatilization. A total of 116 aerosol samples were collected in this study.

pH measurements and analysis of the major WSIIs in the TSPs

The pH values of the samples were measured using a desktop pH meter (Orion STAR A211, Thermo Fisher Scientific, USA) immediately after obtaining the extracted aqueous solution. The remaining aqueous extracts were stored at -20°C until the water-soluble inorganic ions were analyzed.

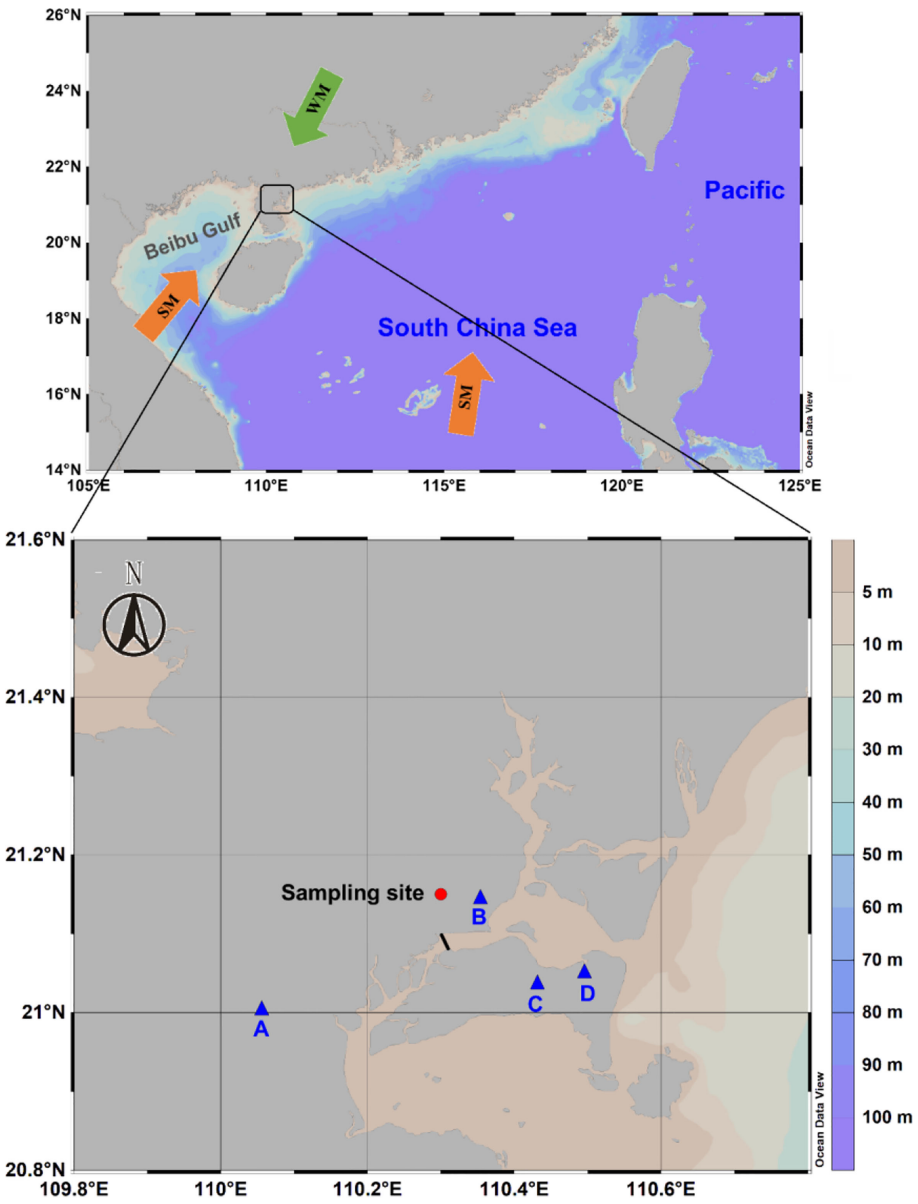

FIGURE 1
The sampling location of Zhanjiang (red dot). WM, winter monsoon; SM, summer monsoon. The blue triangles are the location of heavy industry. A, B, C, and D denote Chenming Paper Mill, Sinopec Zhanjiang Dongxing Petrochemcial Factory, Zhongke (Guangdong) Refinery & Petrochemical Factory, and Baosteel Zhanjiang Iron & Steel Plant, respectively.

Five cations (Mg^{2+}, Ca^{2+}, K^+, Na^+, and NH_4^+) and three anions (Cl^-, NO_3^-, and SO_4^{2-}) in the aqueous extracts of the aerosol samples were analyzed in this study. NH_4^+ and NO_3^- were determined using standard colorimetric methods (Grasshoff et al., 1999), and their detection limits were< 0.1 mg/L. The other ions were analyzed using ion chromatography (Dionex Aquion, Thermo Fisher Scientific), and their uncertainties were< 5%.

Meteorological data

Daily meteorological parameters, i.e., air temperature (°C), wind speed (km/h), and relative humidity (RH, %), were obtained from the local weather station (< 15 km southwest of the sampling site) during the sampling period. The precipitation was documented after each rainfall event. Detailed information on the rainfall sampling protocols can be found in our previously published papers (Chen

et al., 2019; Chen et al., 2020). The daily air pollutants, such as SO_2, NO_2, $PM_{2.5}$, and PM_{10}, presented during the sampling period in Zhanjiang were downloaded from https://www.zq12369.com/. A 72-hour average of the data described above (except for precipitation) was calculated and is presented in Figure 4.

Results

As shown in Figure 2, the mass concentration of the TSPs in the atmosphere ranged from 18.1 to 133.6 μg/m^3, with an average and standard deviation of 56.5 ± 24.3 μg/m^3. The average value of the TSPs falls within the recommended range of the international guidelines (150 to 230 μg/m^3). There were significantly seasonal variations in the mass concentrations of the TSPs (Figure 2 and Table 1). The mass concentration of the TSPs in the dry season (with an average value of 68.5 ± 23.0 μg/m^3; Table 1) were significantly higher than those in the rainy season (with an average value of 44.8 ± 19.2 μg/m^3; Table 1; ANOVA, $p< 0.01$).

The contents of the WSIIs in the TSPs increased in the order of $Mg^{2+} < Ca^{2+} < K^+ < Na^+ < NH_4^+ < Cl^- < NO_3^- < SO_4^{2-}$. SO_4^{2-} was the most abundant anion in the TSPs, followed by NO_3^- and Cl^-, which accounted for 56.2%, 27.2%, and 16.6%, respectively, of the total anions. The predominant cations were Na^+, NH_4^+, and K^+, accounting for 28.8%, 26.8%, and 20.4%, respectively, of the total cations. Similar seasonal variation pattern could be observed in the WSIIs. Significantly higher Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-, and SO_4^{2-} values occurred in the dry season, whereas lower values were observed in the rainy season (Figure 2D; Table 1; ANOVA, $p< 0.01$ for these ions). The mass concentrations of K^+ were stable throughout the sampling campaign (Figure 2B and Table 1; ANOVA, $p > 0.05$).

Discussion

Influences of meteorological factors

The average mass concentration of the TSPs in the rainy season (with an average value of 44.8 ± 19.2 μg/m^3) was 34.6% lower than that in the dry season (with an average of 44.8 ± 23.0 μg/m^3) (ANOVA, $p< 0.01$). The backward air mass trajectories during the same sampling periods in our published study (Luo et al., 2022)

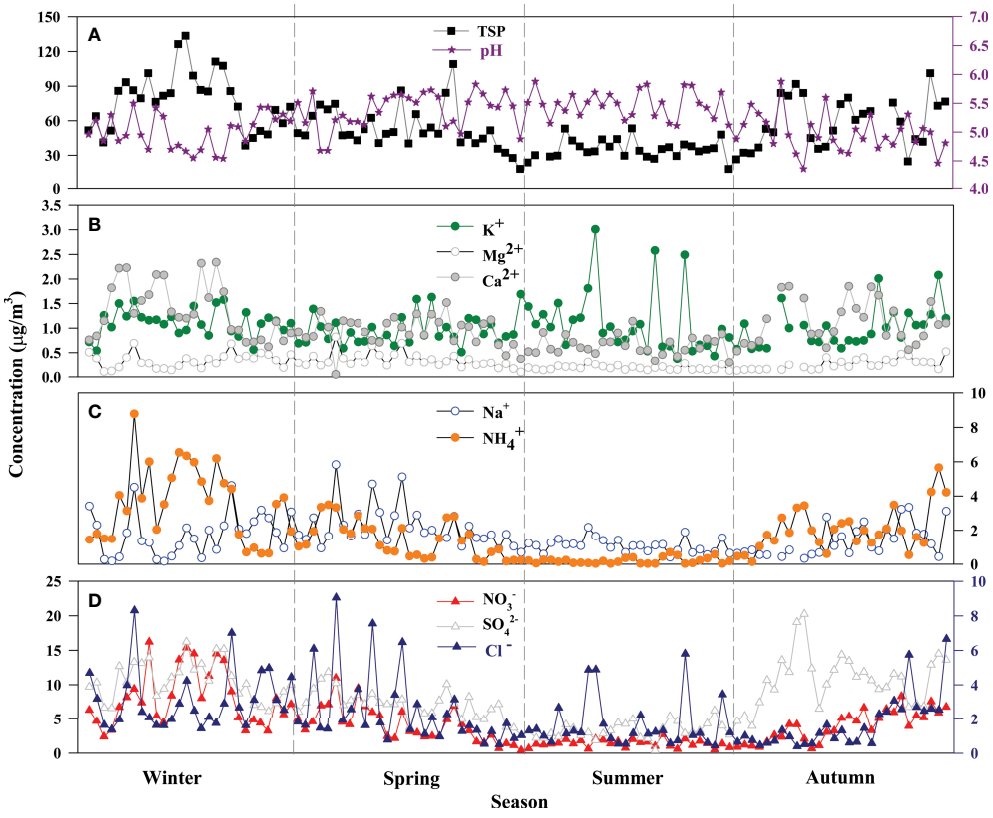

FIGURE 2
Seasonal variations in the pH, and mass concentrations of TSPs and WSIIs (i.e., K^+, Mg^{2+}, Ca^{2+}, Na^+, NH_4^+, NO_3^-, SO_4^{2-} and Cl^-) in the atmospheric aerosols in Zhanjiang.

TABLE 1 Seasonal variations in the WSIIs in the atmospheric aerosols in Zhanjiang.

	Rainy season	Dry season
n	58	58
Rainfall (mm)	1236.5	326.4
TSPs (μg/m^3)	44.8 ± 19.2	68.5 ± 23.0
Na^+ (μg/m^3)	1.3 ± 0.8	1.9 ± 1.2
NH_4^+ ($\mu g/m^3$)	0.7 ± 0.9	2.9 ± 1.8
K^+ (μg/m^3)	1.0 ± 0.5	1.1 ± 0.3
Mg^{2+} (μg/m^3)	0.2 ± 0.1	0.3 ± 0.1
Ca^{2+} (μg/m^3)	0.8 ± 0.4	1.2 ± 0.5
Cl^- (μg/m^3)	1.5 ± 1.3	2.9 ± 1.9
SO_4^{2-} ($\mu g/m^3$)	5.6 ± 3.7	10.3 ± 2.6
NO_3^- ($\mu g/m^3$)	2.0 ± 1.4	6.7 ± 3.5

showed that the air masses during the dry season could bring land-based aerosol to the Zhanjiang and the air parcels during the rainy season were mainly originated from the South China Sea. This suggested that the seasonal variation of TSPs concentrations in Zhanjiang were related to the air masses transition. However, it is hypothesized that this influence might be minor than local influences as discussed in the following sections. In addition, during the rainy season, the TSPs concentrations in the present study were lower than the value in the South China Sea (remote area, 60.4 ± 27.0 μg/m^3; Xiao et al., 2017), Guangzhou (urban area, 62.1 μg/m^3; Tan et al., 2009), and Guiyang (polluted area, 85.4 ± 29.1 μg/m^3; Li Q. et al., 2020). During the dry season, the TSPs concentrations in the present study were significantly lower than the concentration observed in the South China Sea (remote area, 114.7 ± 82.1 μg/m^3; Xiao et al., 2017), Shanghai (urban area, 94.64 μg/m^3; Gao et al., 2011), Xi'an (urban area, 130 μg/m^3; Gao et al., 2011), and Guiyang (polluted area, 140.2 ± 46.2 μg/m^3; Li Q. et al., 2020), and were similar to Guangzhou (urban area, 66.7 μg/m^3; Tan et al., 2009). These results implied that the seasonal variation of TSPs concentrations were greatly influenced by local conditions, for example, meteorological conditions (i.e., precipitation, temperature, wind speed, and RH) and local emissions (Gao et al., 2011; Meng et al., 2016; Xiao et al., 2017). Recent studies also found that local emission and meteorological factor have an important impact on air pollution (Wang et al., 2021; Zhou et al., 2022).

The meteorological conditions can affect chemical conversion and the deposition of TSPs (Meng et al., 2016) and thus affecting the mass fraction of WSIIs in TSPs. During the sampling periods, the mass fraction of WSIIs accounted for 35.7% of TSPs, displaying a higher fraction in the dry season (with an average value of 41.4%) and lower fraction in the rainy season (with an average value of 30.0%). This suggested that the seasonal variation of WSIIs was related to TSPs concentrations. The mass fraction of WSIIs in TSPs in the present study was higher than the value in the South China Sea (24.8%; Xiao et al., 2017), and were comparable to the value in urban Guangzhou (35%; Tao et al., 2017) and in suburban Zhuhai (34%; Tao et al., 2017). The significantly positive relationships between WSIIs and TSPs ($p< 0.01$ for NH_4^+, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}; $p< 0.05$ for Mg^{2+}; $p > 0.01$ for K^+ and Na^+; Table 2) also supported the concept that WSIIs were important constituents of TSPs. Therefore, WSIIs might play a significant role in TSPs in the present study.

During the sampling periods, the WSIIs concentrations were also higher during the dry season and were lower during the rainy season, with an average reduction rate of 42.3% (Table 1). This result is consistent with the seasonal pattern in Guiyang, that is, decreases in the TSPs (decrease of 18%) and WSIIs concentrations during the rainy season (Xiao and Liu, 2004). However, in contrast to the findings for Guiyang, the percentages of SO_4^{2-}, Cl^-, NO_3^-, and NH_{4^+} in the total WSIIs were lower in the rainy season than those in the dry season, indicating that in the particles, these ions tend to be coarser, so they have a shorter residence time than the finer components. Thus, they were readily captured by precipitation and were preferentially scavenged below the clouds (Xiao and Liu, 2004). Notably, in the precipitation characteristics shown in Figure 3, the precipitation frequency (precipitation frequency was calculated from the fraction of rain events in each month during sampling periods; rainfall > 0.5 mm/day as the criterion; Hou et al., 2018; data sourced from https://en.tutiempo.net/world.html) and the amount of rainfall were significantly higher in the rainy season (especially in summer) and lower in the dry season, which further suggests a removal process driven by frequent and large amounts of precipitation (Hou et al., 2018).

Temperature, wind speed, and RH also have impacts on the seasonal variations in the TSPs and WSIIs in atmospheric aerosols (Xiao and Liu, 2004; Xiao et al., 2017). In this study, the TSPs and WSIIs were strongly negatively correlated with the air temperature ($p< 0.01$ for TSPs, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}; $p > 0.05$ for K^+ and Na^+; Table 2), suggesting that the hot and rainy season helps reduce the amount of these particles in the atmosphere, leading to a decrease in the TSPs and WSIIs concentrations (Figure 2 and Table 1). Only the mass concentration of Ca^{2+} in the TSPs was affected by wind speed (Table 2), and the resultant positive correlation (Table 2, $p< 0.05$) suggests that strong winds can bring dust containing Ca^{2+}.

The high RH throughout the year (>80%) in Zhanjiang (Figure 4C) suggested that the particles in the atmospheric aerosols were wet and easily interacted with each other (Xiao and Liu, 2004), leading to an increase in particle size and the dry deposition rate (Tang et al., 2006). If the dry deposition rate increased during the sampling periods, a systematic decrease in the TSPs and WSIIs with increasing RH should be observed, and good correlations should be found among them. By contrast, the TSPs and WSIIs (with the exception of Na^+) were not correlated with RH in Zhanjiang (Table 2), indicating that the increase in particle size caused by the RH had little impact on the dry deposition rate.

TABLE 2 Correlation coefficients between pH, the WSIIs in the atmospheric aerosols, and the meteorological parameters in Zhanjiang.

	TSPs	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH	WS	RH	T
TSPs	1	0.183	0.850**	0.120	0.330*	0.703**	0.293**	0.819**	0.799**	-0.512**	0.101	-0.006	-0.532**
Na^+		1	0.152	0.039	0.948**	-0.216*	0.813**	0.358**	0.136	0.163	0.048	0.212*	-0.146
NH_4^+			1	0.135	0.294**	0.576**	0.335**	0.849**	0.798**	-0.608**	0.083	-0.034	-0.589**
K^+				1	0.069	0.094	0.339**	0.102	0.002	0.004	0.000	-0.058	-0.061
Mg^{2+}					1	-0.029	0.807**	0.473**	0.292**	0.045	0.102	0.175	-0.292**
Ca^{2+}						1	-0.086	0.657**	0.478**	-0.418**	0.234*	-0.164	-0.535**
Cl^-							1	0.426**	0.158	0.088	0.084	0.124	-0.298**
NO_3^-								1	0.657**	-0.539**	0.144	0.000	-0.638**
SO_4^{2-}									1	-0.680**	0.049	-0.129	-0.447**
pH										1	-0.064	0.294**	0.340**

WS, wind speed (km/h), RH, relative humidity (%); T, air temperature (°C); **: correlation at the 0.01 level (two-tailed); *: correlation at the 0.05 level (two-tailed).

Indicators of aerosol acidity

In addition to the TSP and WSII concentrations, aerosol acidity is also a concerning environmental problem. Thus, the ion balance and neutralization factors were calculated to investigate the aerosol acidity (Xu J. S. et al., 2017; Agarwal et al., 2020). In order to evaluate the acid–base balance of the ions in the atmospheric aerosols, ion balance calculations, i.e., the ratio of the total anion equivalents to the total cations equivalents (Σ_{AE}/Σ_{CE}), have generally been conducted in previous studies (Zhang et al., 2011; Xu J. S. et al., 2017; Agarwal et al., 2020). The charge balance between the anions and cations was calculated as follows:

$$\Sigma_{AE} = [SO_4^{2-}]/48 + [NO_3^-]/62 + [Cl^-]/35.5, \quad (1)$$

$$\Sigma_{CE} = [Na^+]/23 + [NH_4^+]/18 + [K^+]/39 + [Mg^{2+}]/12 + [Ca^{2+}]/20. \quad (2)$$

Here, $[SO_4^{2-}]$, $[NO_3^-]$, $[Cl^-]$, $[Na^+]$, $[NH_4^+]$, $[K^+]$, $[Mg^{2+}]$, and $[Ca^{2+}]$ refer to the mass concentrations of the ions (μg/m^3).

The plot of Σ_{AE} vs Σ_{CE} is presented in Figure 5A. The slope of the linear regression for all of the TSP samples (R^2 = 0.87) was slightly higher than 1, indicating a cation deficient scenario, which may be the result of the omission of hydrogen ions from the calculations (Zhang et al., 2011). Furthermore, the average ratio of Σ_{AE}/Σ_{CE} in the four

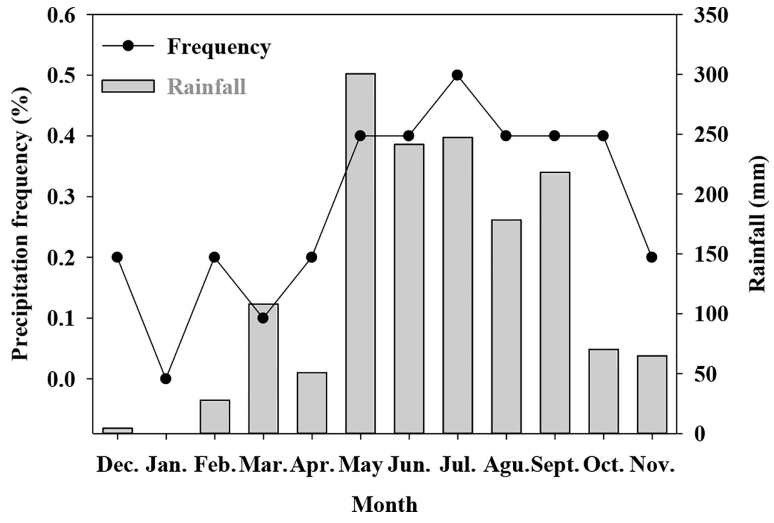

FIGURE 3
Monthly precipitation frequency and total rainfall amount in Zhanjiang. Precipitation frequency data was calculated from the fraction of rain events in each month during sampling periods (rainfall > 0.5 mm/day as the criterion; Hou et al., 2018; data sourced from https://en.tutiempo.net/world.html).

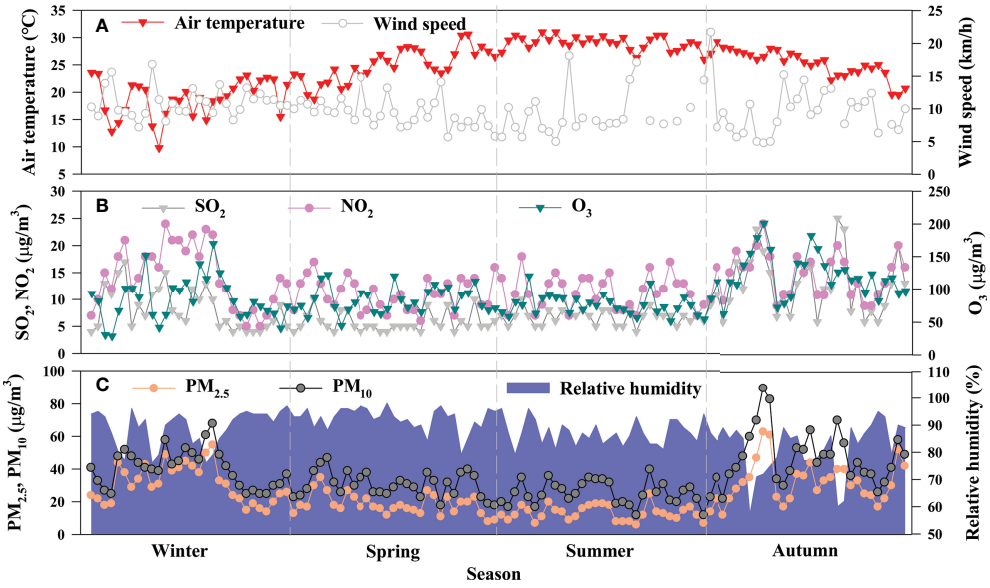

FIGURE 4
72-hour average values of air temperature, wind speed, SO_2, NO_2, O_3, $PM_{2.5}$, PM_{10}, and relative humidity in Zhanjiang.

seasons followed the order autumn (1.34) > winter (1.12) > summer (1.03) > spring (1.02), which is in good agreement with the seasonal pattern of the pH values (Figure 2A). Therefore, these results demonstrate that the aerosols are more acidic in autumn and winter and are less acidic in spring and summer in Zhanjiang. This seasonal variation is consistent with the aerosol research conducted in Guangzhou (GZ) and Hong Kong (HK), where the samples were found to have lower pH values (pH = 4.33 and 5.21 in GZ and HK, respectively) in winter and higher pH values (pH = 5.21 and 5.72 in GZ and HK, respectively) in summer (Cao et al., 2013).

The ratio of the NH_4^+ equivalent concentration to the sum of the equivalent SO_4^{2-} and NO_3^- concentrations (i.e., $[NH_4^+]/[SO_4^{2-}+NO_3^-]$) in the TSPs can be used to assess the neutralization reaction (secondary aerosol process) among NH_4^+, SO_4^{2-}, and NO_3^- (Xu J. S. et al., 2017). In this study, the equivalent ratios of $[NH_4^+]/[SO_4^{2-}+NO_3^-]$ of the samples were less than 1:1 (Figure 5B), which indicates an NH_4^+ deficiency in the ambient particles (Zhou et al., 2018). However, the measurements in this region are comparable to those on Jeju Island (average 1.7 ± 1.1 μg/m^3; Kundu et al., 2010) and in Guiyang (average 3.81 ± 1.64 μg/m^3; Xiao and Liu, 2004), are higher than those in Yurihonjo

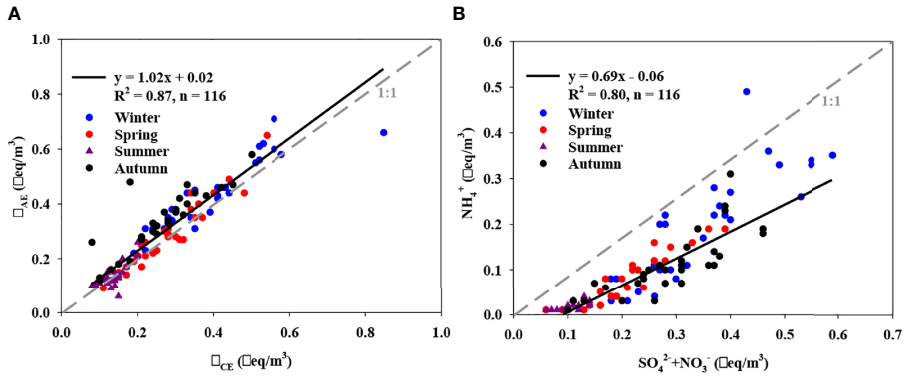

FIGURE 5
(A) Ion balance of the TSPs in Zhanjiang. **(B)** Relationship between the equivalent NH_4^+ concentration and the sum of the equivalent SO_4^{2-} + NO_3^- concentrations in the TSPs in Zhanjiang.

(rural site in Japan, average 0.38 ± 0.33 μg/m^3; Kawashima and Kurahashi, 2011) and NH_4^+ inadequate ambient (Jickells et al., 2003; Lin et al., 2016). This demonstrates that the NH_4^+ in the atmosphere in Zhanjiang is adequate. One possible reason for this discrepancy is that the equivalent concentrations of the acidifying anions were considerably more abundant. That is, SO_4^{2-} and NO_3^- were too abundant for the NH_4^+ in the atmospheric aerosols to be neutralized, and thus the acid status of the atmospheric aerosols can be ascribed to an excess of acidifying anions (Cao et al., 2020). Thus, the higher acidity in autumn and winter could be related to the higher concentrations of SO_4^{2-} and NO_3^- (Figure 2D).

Cations (NH_4^+, nss-K$^+$, nss-Mg^{2+}, and nss-Ca^{2+}) have individual neutralization capacities, and NH_4^+ plays a major role in decreasing aerosol acidity (Xu J. S. et al., 2017; Agarwal et al., 2020). Based on the similar mass concentrations of the cations in this study (Figure 2A–C), we hypothesize that there were other major neutralization ions in addition to NH_4^+. Thus, the neutralization factors (NFs) were investigated to determine the dominant neutralization cations. The contributions of Na$^+$ and Cl$^-$ to lessening the aerosol acidity are considered to be negligible since they are mainly sourced from sea salts (Safai et al., 2010; Satsangi et al., 2013). Although a good correlation was observed between Na$^+$ and Cl$^-$ ($p< 0.01$; Table 2), the corresponding ratios of [Na$^+$]/[Cl$^-$] were found to be lower than that of seawater (1.1) (Xu et al., 2014), suggesting that coal combustion was also a source of Cl$^-$ in addition to sea salt (Xue et al., 2016; Jain et al., 2017; Xu J. S.et al., 2017). Therefore, the contribution of Cl$^-$ to the neutralization should be taken into account, and the non-sea salt Cl$^-$ ([nss-Cl$^-$]) can be calculated by subtracting the sea salt Cl$^-$ ([ss-Cl$^-$] = [Na$^+$]/1.1). NFs in Zhanjiang were calculated using the following equations:

$$NF(NH_4^+) = [NH_4^+]/([NO_3^-] + [nss - Cl^-] + [nss - SO_4^{2-}]), \quad (3)$$

$$NF(nss - K^+) = [nss - K^+]/([NO_3^-] + [nss - Cl^-] + [nss - SO_4^{2-}]), \quad (4)$$

$$NF(nss - Mg^{2+}) = [nss - Mg^{2+}]/(2[NO_3^-] + 2[nss - Cl^-] + [nss - SO_4^{2-}]), \quad (5)$$

$$NF(nss - Ca^{2+}) = [nss - Ca^{2+}]/(2[NO_3^-] + 2[nss - Cl^-] + [nss - SO_4^{2-}]). \quad (6)$$

Here, $[NH_4^+]$, $[NO_3^-]$, [nss-Cl$^-$], $[nss - SO_4^{2-}]$, [nss-K$^+$], [nss-Mg^{2+}], and [nss-Ca^{2+}] refer to the mass concentration of the ions (μg/m^3). For cases with [Na$^+$]/[Cl$^-$] ratios higher than 1.1, [Cl$^-$] should be substituted for [nss-Cl$^-$]. The non-sea salt ions were calculated as follows (Balasubramanian et al., 2003; Nair et al., 2005):

$$[nss - K^+] = [K^+] - [Na^+] * 0.037, \quad (7)$$

$$[nss - Mg^{2+}] = [Mg^{2+}] - [Na^+] * 0.12, \quad (8)$$

$$[nss - Ca^{2+}] = [Ca^{2+}] - [Na^+] * 0.0385. \quad (9)$$

The NF values of the four cations (NH_4^+, nss-K$^+$, nss-Mg^{2+}, and nss-Ca^{2+}) are listed in Table 3. As speculated, there were three major neutralization ions in Zhanjiang. Nss-K$^+$ was the major neutralization ion in summer, which may be related to the fact that biomass burning is an important anthropogenic activity in rural sites (Xu J. S. et al., 2017; Agarwal et al., 2020). The NF values of NH_4^+ were the highest in winter, spring, and autumn, suggesting its dominant impact in neutralizing aerosol acidity. This result is supported by a previous study (Xu J. S. et al., 2017). Nss-Ca^{2+} was the second largest contributor to the neutralization of aerosol acidity, possibly due to the enhanced soil dust brought by strong wind, as suggested by the significant positive correlation between Ca^{2+} and the wind speed ($p< 0.01$; Table 2). Nearby agricultural fields and unpaved roads (Xu J. S. et al., 2017; Agarwal et al., 2020) could be the origins of this soil dust. The NF values of nss-Mg^{2+} were the lowest during the sampling periods, indicating that it had a minor neutralization effect.

The role of precipitation in chemical conversions

As was previously discussed, in this study, the aerosol acidity and concentration were correlated with excess NO_3^- and SO_4^{2-}. Knowledge of the origin and processes of these ions could help lessen aerosol pollution. Aerosol acidity is greatly affected by the

TABLE 3 The neutralization factors (NFs), i.e., NH_4^+, nss-K$^+$, nss-Mg^{2+}, and nss-Ca^{2+}, in the TSPs in Zhanjiang.

	NH_4^+	nss-K$^+$	nss-Mg^{2+}	nss-Ca^{2+}
Winter	0.11	0.04	0.01	0.05
Spring	0.07	0.06	0.01	0.06
Summer	0.02	0.20	0.01	0.09
Autumn	0.07	0.04	0.01	0.06
Average	0.07	0.08	0.01	0.07

oxidation of nitric oxide (NOx) to NO_3^- and of sulfur dioxide (SO_2) to SO_4^{2-} in the atmosphere (Cao et al., 2020). The nitrogen oxidation ratio (NOR) and the sulfur oxidation ratio (SOR) J. S. were estimated using the following equations (Lin, 2002; Xu et al., 2017) in order to gain a better understanding of the conversions of NO_3^- and SO_4^{2-}:

$$SOR = [nss - SO_4^{2-}]/([nss - SO_4^{2-}] + [SO_2]), \quad (10)$$

$$NOR = [NO_3^-]/([NO_3^-] + [NO_2]) \quad (11)$$

Here, $[nss - SO_4^{2-}]$, $[SO_2]$, $[NO_3^-]$, and $[NO_2]$ refer to the mass concentrations of the ions (μg/m^3). The higher SOR and NOR values observed (threshold: 0.1) suggest the presence of more gaseous precursors that generate sulfate- and nitrate-containing secondary aerosols through oxidation (Colbeck and Harrison, 1984; Ohta and Okita, 1990; Kaneyasu et al., 1995).

The monthly and seasonal variations in air temperature, NOR, SOR, and the amount of rainfall are presented in Figure 6. As can be seen, the monthly average values of NOR and SOR were higher than 0.1, indicating a considerable conversion of gaseous precursors to NO_3^- and SO_4^{2-} in the atmospheric aerosols during the sampling periods. The fact that NO_2 and SO_2 were relatively abundant in winter and autumn (Figure 4B) could contribute to the higher occurrences of NO_3^- and SO_4^{2-} (Figure 2D), which were seasonally consistent with the lower pH values (Figure 2A). The decreased production of secondary aerosols in summer is indicated by the valleys in the SOR and NOR curves (Figure 6). This seasonal pattern is contrary to the results of previous studies (Zhang et al., 2011; Xu J. S. et al., 2020). The ambient oxidant (O_3) for chemical conversion is relatively abundant (Figure 4B), so the different meteorological conditions may be the cause of the low conversion rates. The conversion of NO_2 to NO_3^- and SO_2 to SO_4^{2-} is favored by warm and humid ambient conditions (Zhang et al., 2011; Xu J. S. et al., 2020). Since the city investigated in this study is warmer and moister than Xi'an (Zhang et al., 2011), the chemical conversion of NO_2 and SO_2 occurred year-round, and the calculated oxidation ratio was higher than that in the abovementioned area. Additionally, the amount of rainfall in Zhanjiang is about twice than that in the abovementioned area and is mainly concentrated in summer (Figure 4), which gives rise to a precipitation-driven removal process. Therefore, the coexistence of low gaseous precursors (Figure 4B), low precursor conversions (Figure 6), and frequent plentiful rainfall (Figure 3) in summer in Zhanjiang may be related to the removal effect caused by the precipitation. Gaseous precursors can be captured by precipitation below the clouds (Chen et al., 2020), and a lack of reactants may induce low oxidation ratios (Jiang, 2016).

It has been reported that gaseous precursors are predominantly emitted by fossil fuel combustion (> 70%; Lv, 2019; Liu et al., 2019), and high concentrations of NO_2 and SO_2 in winter are influenced by additional coal combustion for heating (Zhang et al., 2011). Thus, the reduction in NO_2 and SO_2 in summer seems to suggest a decrease in fossil fuel usage in addition to the removal effect caused by precipitation. However, we believe that the reduced combustion in summer is unlikely to be based on the ratio of NO_3^- to SO_4^{2-} (NO_3^-/SO_4^{2-}) and power production.

The NO_3^-/SO_4^{2-} ratio of the atmospheric aerosols is recognized as an effective approach to assessing stationary and mobile sources of nitrogen and sulfur and has been widely used at various locations around the world (Arimoto et al., 1996; Tan et al., 2009; Safai et al., 2010; Begam et al., 2017). When this ratio is > 1, the emissions are considered to be produced by mobile sources; otherwise, they are emitted from stationary sources

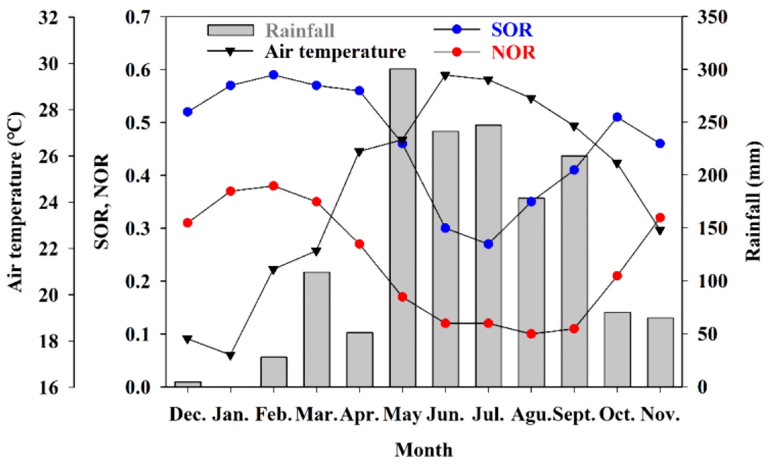

FIGURE 6
Monthly average values of air temperature, NOR, SOR, and amount of rainfall.

(Arimoto et al., 1996; Lv, 2019). As can be seen from Figure 7, the monthly average NO_3^-/SO_4^{2-} ratios during the sampling periods were<1 (from 0.05 to 2.57, averaged at of 0.55 ± 0.33), indicating that the predominance of stationary sources over mobile sources in Zhanjiang. Thus, the NO_2 and SO_2 in the atmosphere during the sampling periods were associated with local emissions.

China is a coal-fired country, and more than half of the coal is consumed by electric power plants, so power production can be considered to be an indicator of the local fossil fuel consumption. Power production continues at a high rate in summer; whereas it has a relatively low rate in winter and autumn (Figure 7), implying an adequate amount of gaseous precursors should be present in the hot and rainy season. However, the observations in summer showed low values (Figure 4B), which in turn supports the possibility of a precipitation-driven removal process.

Possible air quality improvement process and source identification in a heavy industry coastal city

Aerosol pollution is a significant global problem caused by rapid economic and industrial development. The inconsistency between heavy industrial activities and low aerosol concentrations during our sampling campaign in Zhanjiang may be related to a precipitation-driven removal effect (Hou et al., 2018) and the marine dilution effect. Aerosols from marine emissions are considered to be relatively clean (Jickells et al., 2003; Xiao et al., 2017; Zhou et al., 2019), which results in potential dilution and air quality improvement when mixed with polluted aerosols produced by terrestrial anthropogenic activities. Since the study area is bordered by the SCS, the marine effect should be taken into account in this region. Thus, the aerosols from non-sea salt contributions were evaluated, and the results are presented in Table 4. More than 50% of the Mg^{2+} in Zhanjiang was sourced from sea salt (Table 4), indicating that the Mg^{2+} is predominantly from marine emissions. The higher ratios (>90%) of nss-K^+/K^+, nss-Ca^{2+}/Ca^{2+}, and $nss-SO_4^{2-}/SO_4^{2-}$ found during sampling campaign (Table 4) indicate minor contributions from marine emissions to these WSIIs in the aerosols.

In order to investigate the effects of precipitation on the TSPs, linear regression analysis (SPSS version 22.0, IBM Corp.) was conducted to quantitatively describe the impacts of precipitation on the TSPs. The frequency and amount of precipitation were selected as the precipitation characteristics, as was suggested by Hou et al. (2018). As can be seen from the data shown in Figure 8, the TSPs were negatively affected by precipitation, indicating that the atmospheric aerosol lifetime was sensitive to precipitation (Hou et al., 2018), and precipitation significantly contributed (> 50%) to the decrease in the TSPs pollution in Zhanjiang. The high coefficient of determination (R^2 = 0.63) in Figure 8A further suggests that the precipitation frequency had a larger effect on the removal efficiency than the amount of precipitation. The model results of Hou et al. (2018) also highlight the importance of precipitation frequency in shortening aerosol lifetime.

Principal component analysis (PCA, SPSS version 22.0, IBM Corp.) was conducted in this study and presented in Table 5. Principal Components Analysis (PCA) is an algorithm to

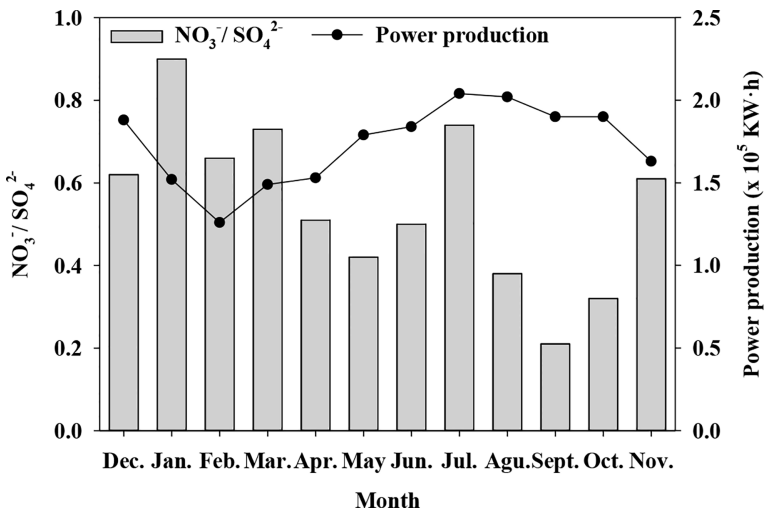

FIGURE 7
Monthly average values of the NO_3/SO_4^2 ratio (mass concentration ratio) and power production in Zhanjiang during the sampling periods (data from the Zhanjiang Bureau of Statistics, https://www.zhanjiang.gov.cn/tjj/).

TABLE 4 Non-sea salt ionic fractions in Zhanjiang.

	nss-K^+/K^+	nss-Mg^{2+}/Mg^{2+}	nss-Ca^{2+}/Ca^{2+}	$nss-SO_4^{2-}/SO_4^{2-}$
Winter	93%	45%	93%	96%
Spring	91%	27%	91%	92%
Summer	96%	33%	93%	89%
Autumn	94%	44%	94%	96%
Average	94%	37%	93%	93%

transform the columns of a dataset into a new set of features called Principal Components (PC). According to the results of PCA, a large chunk of the information across the full dataset is effectively compressed in fewer feature columns (i.e., PC1, PC2, PC3, etc.), while still preserving as much information as possible. This enables dimensionality reduction and ability to visualize the separation of classes or clusters (https://builtin.com/data-science/step-step-explanation-principal-component-analysis). The extracted PC with eigenvalue > 1.0 is retained for interpretation and the loading above 0.5 of each component is determined to be the major contribution to each of the PC scores (Gao et al., 2011; Zhang et al., 2011; Agarwal et al., 2020; Liu et al., 2021a; Liu et al., 2021b). In these studies, the determined component is regarded as tracer of certain source (Gao et al., 2011; Zhang et al., 2011; Agarwal et al., 2020; Liu et al., 2021a; Liu et al., 2021b). Similarly, the determined component can be used for tracing sources in the present study.

As presented in Table 5, three factors were identified (eigenvalue > 1.0) as PCs and accounted for 90.0% of the total data variance. PC1 was strongly loaded with TSPs, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. NH_4^+, NO_3^-, and SO_4^{2-} were mainly from a secondary formation process (Agarwal et al., 2020). As was previously discussed, Cl^- reflects the influence of coal combustion (Xue et al., 2016; Jain et al., 2017; Xu J.S. et al., 2017). Ca^{2+} and Mg^{2+} reflect the contributions of soil dust and are the principal crustal elements (Gao et al., 2011; Zhang et al., 2011; Meng et al., 2016; Saxena et al., 2017; Jaiprakash et al., 2017). Therefore, PC1 was identified as a mixture of secondary aerosols, coal combustion, and soil dust. PC2 explained 27.4% of the total variance and was observed to be heavily loaded for Na^+, Mg^{2+}, and Cl^-, which were possibly influenced by sea salts. This is in agreement with the results for other coastal areas (Xu J. S. et al., 2017), that is, the aerosols in these areas exhibited oceanic characteristics. Thus, the presence of these ions indicates that PC2 was primarily sourced from marine emissions. PC3 was characterized by a high loading of K^+ and accounted for 11.5% of the variance. Moreover, K^+ was found to be uncorrelated with most of the WSIIs in Zhanjiang (Table 2), suggesting that the PC3 source is biomass burning.

We summarize the possible removal effect of TSPs in Zhanjiang in a conceptual diagram (Figure 9), showing frequent precipitation could remove a large amount of gas precursors and local secondary aerosols. The aerosols sourced from clean marine emissions therefore act as the supplement in the ambient, leading to the observance of relatively high contribution in the TSPs. This result may provide useful information for lessening aerosol pollution under the background of the pervasive anthropogenic aerosols pollution around the world, and the relocation site chosen for industrial activities.

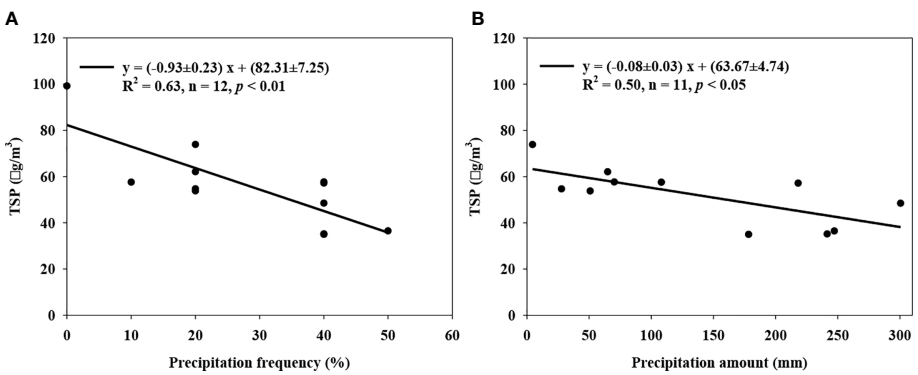

FIGURE 8
Linear regressions of **(A)** TSPs and precipitation frequency and **(B)** TSPs and amount of precipitation.

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TABLE 5 The results of the PCA for the mass concentrations of the TSPs and WSIIs in Zhanjiang.

	PC1	PC2	PC3
TSPs	**0.894**	-0.318	0.000
Na^+	0.496	**0.825**	-0.188
NH_4^+	**0.880**	-0.302	0.038
K^+	0.196	0.154	**0.959**
Mg^{2+}	**0.632**	**0.710**	-0.170
Ca^{2+}	**0.574**	-0.641	0.059
Cl^-	**0.598**	**0.710**	0.170
NO_3^-	**0.898**	-0.098	-0.055
SO_4^{2-}	**0.813**	-0.377	-0.132
Eigenvalue	4.413	2.468	1.038
% of variance	49.033	27.418	11.532
Cumulative variance	49.033	76.451	89.983
Factors	Secondary aerosol, coal combustion, and soil dust	Marine emission	Biomass burning

The bold values indicate strong loadings.

As stated above, gas precursors and local secondary aerosols can be captured by frequent precipitation and abundant rainfall. These materials thus enter the marine environment in the coastal area as atmospheric deposition, which may aggravate nutrients loading and even result in eutrophication and hypoxia (Duce et al., 2008; Chen et al., 2017; Wu et al., 2018; Cui et al., 2020). The impacts of atmospheric deposition on marine environment require attention and need further exploration.

Conclusions

The goal of this study was to clarify the discrepancy between industrial activities and low aerosol concentrations in a tropical coastal city due to a precipitation-driven removal process and the marine dilution effect. In Zhanjiang, 72h TSPs collection and WSIIs analysis were conducted during a one-year sampling campaign. The results of this investigation show that the TSP mass concentrations and the total WSII

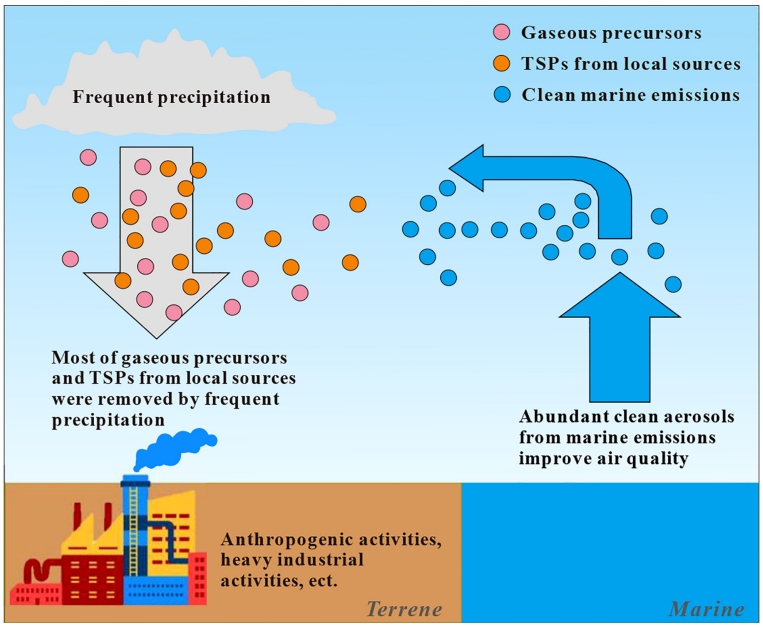

FIGURE 9
Conceptual diagram for TSPs removal process in Zhanjiang.

concentrations in Zhanjiang were lower in the spring and summer and were higher in the winter and autumn. This seasonal pattern and high aerosol acidity (indicated by the ion balance, neutralization factors, and pH values) further suggest that the TSPs, WSIIs, and acidic gaseous precursors were removed by frequent precipitation and abundant rainfall. The PCA results revealed that secondary aerosols and sea salts were important sources of the TSPs and WSIIs. One of the more significant findings of this study is that a combination of high precipitation frequency and marine dilution can lessen aerosol pollution in a heavy industrial city.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

XZ Conceptualization, Writing-Original draft, Writing-Review and Editing. Data Curation, Visualization, Software. ZL Methodology, Project administration, Writing-Review and Editing. CC Investigation, Methodology, Writing-Review and Editing. HL Investigation, Writing-Review and Editing. QZ Methodology, Project administration, Writing-Review and Editing. ZZ Methodology, Writing-Review and Editing. QL Writing-Review and Editing. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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